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**Kinetics of Copolymerization. III.
Determination of the Rate of Initiation in the
Copolymerization System Acrylonitrile/Methyl
Acrylate/Dimethylformamide**

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ABSTRACT

For the AIBN-initiated copolymerization system acrylonitrile/methyl methacrylate/dimethylformamide, the dependence of the composition of the monomer mixture on the rate constant of initiation and that of the initiator decomposition has been investigated at 313, 323, and 333°K. It was established that the rate constant of initiator decomposition is independent of, while that of the initiation is dependent on, the composition of the monomer mixture. The efficiency of initiation has been calculated and its value was found to be somewhat altered not only by the composition of the monomer mixture but also decreased slightly with an increase of temperature.

INTRODUCTION

For the kinetic treatment of copolymerization reactions, similarly to the case of homopolymerization, the rate of initiation and its dependence on the reaction medium must be known.

In the copolymerization literature, surprisingly little work can be found where the rate of initiation and the effect of the medium have been directly measured or investigated. In the majority of copolymerization systems, the rate of initiation was assumed to be independent of monomer composition or it was calculated from the polymerization data by supposing additivity [see, e.g., Refs. 1-3]. Melville and his co-workers [4, 5], however, as early as the 1950s drew attention to the great dependence of the rate of initiation on the medium in the copolymerization of styrene with butyl acrylate. Similar dependencies on the composition were found later with some other copolymerization systems [6-8]. The rate of initiation was concluded indirectly from the rate or degree of polymerization. This method requires, however, the careful consideration of possible errors even when a labeled initiator is used [8-10].

The rate of initiation in the copolymerizing system styrene/diethyl maleate was measured with the direct, inhibition kinetic method by Tüdös et al. [11]. Using a stable free radical as inhibitor, they found a very high (about 100%) variation of the rate constant of initiation with the initial monomer composition. That is why the direct measurement of the rate of initiation should not be omitted in precise polymerization kinetic investigations.

The present paper deals with the investigation of the copolymerization system acrylonitrile/methyl acrylate/dimethylformamide (AN/MA/DMF). For the rate of initiation of this system, no data can be found in the literature.

The rate constant of initiation ($2k_{if}$) was determined by inhibition method at different initial monomer compositions at 313, 323 and 333°K using the Banfield radical. The decomposition rate constant (k_1) of azoisobutyronitrile (AIBN) initiation was directly measured by volumetric determination of the nitrogen evolved.

EXPERIMENTAL

Materials Used

Purifications of AN, DMF, and AIBN were given earlier [12]. The inhibitor was removed from MA by several extractions with 10% NaOH solution, then the monomer was washed alkaline-free with water and dried over CaCl_2 . Finally, it was rectified on a column of about 25 theoretical plates. For each series of experiments, freshly distilled MA was used. Physical data of the purified monomer: bp 301°K at 100 torr, 312°K at 150 torr, n_D^{20} 1.4024.

The Banfield radical, used as the inhibitor, was prepared as given in Ref. 13.

Experimental Methods

The inhibition kinetic measurements were performed dilatometrically.

Monomer mixtures of suitable compositions and concentrations were previously prepared in normal flasks and poured into the dilatometers containing precisely weighed quantities of initiator and inhibitor. The mixture to be polymerized was freed from oxygen by the well-known freeze and thaw method. Kinetic measurements were performed at 313, 323, and 333° K. The procedure was followed by the temporal changes in the volumes of monomer mixtures in the dilatometers.

Determination of Decomposition Rate Constant of AIBN

For these measurements, 10 mL ground joint ampules were used into which the suitable quantity of AIBN and 10 mL of monomer, solvent, or monomer mixture of the given composition were added. The monomer mixtures were previously treated with a small quantity of Banfield radical in order to prevent an increase of viscosity. The inhibitor hinders the polymerization without affecting the kinetics of AIBN decomposition [14]. The ampule was connected to the azotometer and put into the thermostat of proper temperature (313, 323, or 333° K). The system was deoxygenated by purified argon flow [15]. The calibrated gas burette was also thermostated at the corresponding temperature. The volume of nitrogen evolved at AIBN decomposition was determined with a precision of ± 0.01 mL.

EXPERIMENTAL RESULTS AND THEIR EVALUATION

Determination of the Rate Constant of Initiation

As mentioned above, the rate constant of initiation ($2k_i f$) in the case of the system AN/MA/AIBN/DMF was determined by inhibition. Using a stable free radical, the rate constant of initiation can be determined from inhibition kinetic data by [16]

$$t_i = \frac{z_0}{2k_1 f \bar{x}} \quad (1)$$

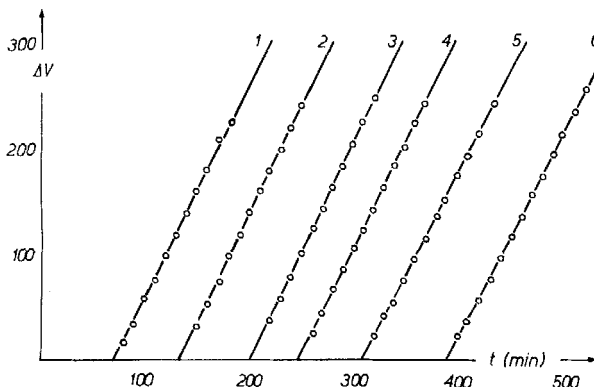


FIG. 1. Polymerization kinetic curves of the system AN/MA/AIBN/DMF/Banfield radical/323°K at different inhibitor concentrations: $x_{MA} = 0.25$ (see Table 2).

where t_i is the length of the inhibition period, z_0 is the initial concentration of inhibitor, \bar{x} is the average concentration of initiator, k_1 is the rate constant of initiator decomposition, and f is the efficiency factor of initiation.

The total initial concentration of monomers ($m_{AN} + m_{MA} = 3.8$ mole/L [12]) was kept constant in the inhibition kinetic measurements while the monomer ratio was varied. From the data obtained in the dilatometric measurements, ΔV vs t relationships were constructed ($\Delta V = V_0 - V_t$, the contraction belonging to moment t). A typical example of such relationships is shown in Fig. 1. The length of the inhibition period (t_i) was determined by the extrapolation of the stationary section of this relation to $\Delta V = 0$. The results of the experiments are listed in Tables 1, 2, and 3.

In the experiments at 313 and 323°K, the $t_i = f(z_0/\bar{x})$ dependencies show a good linearity (see Fig. 2), which indicates simple, one-step inhibition. From the slope of these straight lines, the value of $2k_1f$ can be calculated.

In the experiments at 333°K, however, the dependence of t_i on the inhibitor concentration is not completely linear but involves some other inhibitor-consuming reaction in the system in addition to inhibition. It was found earlier that at higher temperatures the Banfield radical reacts not only with the propagating radical, but also with the monomer, even though with a small rate [12, 16]. In this case the experimental data can be linearized by [12]

TABLE 1. Kinetic Data of the System AN/MA/AIBN/ DMF/Banfield Radical/313° K

X_{MA}	$z_0 \times 10^4$ (mole/L)	$\bar{x} \times 10^2$ (mole/L)	t_i (min)	$\frac{z_0}{\bar{x}} \times 10^3$	$2k_1 \times 10^5$ (min ⁻¹)
0	6.190	8.88	155	6.97	4.183
	7.110	8.87	194	8.02	
	8.870	8.86	252	10.01	
	13.450	8.84	368	15.22	
0.10	3.040	8.94	82	3.40	4.191
	6.545	9.01	172	7.27	
	8.410	8.95	220	9.40	
	9.890	9.04	264	10.93	
	12.890	8.98	344	14.35	
0.50	6.230	8.90	145	7.00	4.618
	7.460	8.92	187	8.36	
	10.220	8.90	260	11.50	
	13.160	8.92	311	14.76	
0.75	2.380	8.92	55	2.67	4.560
	8.310	8.92	187	9.31	
	9.730	8.90	256	10.92	
	11.940	8.90	305	13.41	

$$\left[\frac{z_0}{t_i \bar{x}} \right]^{3/2} = (2k_1 f)^{3/2} \left[1 + 0.74 \alpha \frac{z_0}{\bar{x}} \right] \quad (2)$$

If the data of our copolymerization system at 333° K (see Table 3) are plotted according to Eq. (2) (see Fig. 3), a straight line is obtained for each series, and from the intercept of the line the value of $2k_1 f$ can be calculated.

The rate constants of initiation of the copolymerization systems studied are listed in the last columns of Tables 1, 2, and 3. The dependencies of these values on the initial monomer composition:

TABLE 2. Kinetic Data of the System AN/MA/DMF/AIBN/Banfield Radical/323°K

X_{MA}	$z_0 \times 10^4$ (mole/L)	$x \times 10^2$ (mole/L)	t_i (min)	$\frac{z_0}{\bar{x}} \times 10^2$	$2k_1 f \times 10^4$ (min^{-1})
0.10	2.065	2.070	56	0.998	1.809
	4.327	2.061	114	2.099	
	6.954	2.050	188	3.392	
	7.980	2.044	220	3.904	
	9.929	2.037	269	4.874	
	12.320	2.028	334	6.075	
	14.307	2.021	382	7.079	
	15.409	2.015	415	7.647	
0.25	2.653	2.072	72	1.280	1.862
	5.175	2.063	133	2.508	
	7.641	2.053	200	3.772	
	9.519	2.046	247	4.652	
	11.716	2.037	308	5.752	
	14.784	2.026	390	7.297	
0.50	3.556	2.071	86	1.717	1.882
	4.857	2.063	128	2.535	
	7.238	2.056	186	3.520	
	9.152	2.048	240	4.469	
	12.710	2.033	339	6.252	
	15.702	2.021	415	7.769	
	15.736	2.022	409	7.782	
0.65	2.369	2.060	61	1.150	1.880
	4.854	2.049	127	2.368	
	7.536	2.039	196	3.696	
	8.374	2.036	218	4.113	
	10.475	2.028	274	5.165	
	13.360	2.017	352	6.624	
	16.653	2.005	436	8.306	
	16.486	2.002	446	8.235	

(continued)

TABLE 2. (continued)

x_{MA}	$z_0 \times 10^4$ (mole/L)	$\bar{x} \times 10^2$ (mole/L)	t_i (min)	$\frac{z_0}{\bar{x}} \times 10^2$	$2k_1f \times 10^4$ (min^{-1})
0.90	3.043	2.041	85	1.491	1.878
	5.190	2.030	141	2.560	
	7.872	2.019	218	3.899	
	8.058	2.018	227	3.993	
	10.611	2.009	291	5.282	
	14.429	1.995	384	7.233	
	16.314	1.987	438	8.210	
	18.241	1.982	472	9.203	

^aIn the case of $x_{MA} = 0$, $2k_1f = 1.764$ [12]; in the case of $x_{MA} = 1$, $2k_1f = 1.880$ [17].

TABLE 3. Kinetic Data of the System AN/MA/DMF/AIBN/Banfield Radical/333°K

x_{MA}	$z_0 \times 10^4$ (mole/L)	$\bar{x} \times 10^3$ (mole/L)	t_i (min)	$\frac{z_0}{\bar{x}} \times 10^2$	$2k_1f \times 10^4$ (min^{-1})
0	3.043	3.528	102	8.625	7.78
	5.187	3.452	168	15.026	
	9.628	3.317	292	29.025	
	12.549	3.329	364	38.743	
0.099	1.695	3.749	55	4.522	7.90
	3.835	3.670	119	10.449	
	5.254	3.632	158	14.467	
	8.150	3.534	236	23.061	
	10.468	3.449	296	30.352	
0.234	3.646	3.359	93	7.880	7.92
	5.537	3.259	186	16.990	
	8.770	3.160	280	27.753	
	11.284	3.091	348	36.507	

(continued)

TABLE 3. (continued)

x_{MA}	$z_0 \times 10^4$ (mole/L)	$\bar{x} \times 10^3$ (mole/L)	t_i (min)	$\frac{z_0}{\bar{x}} \times 10^2$	$2k_1 f \times 10^4$ (min^{-1})
0.479	2.998	3.315	107	9.045	8.02
	5.051	3.233	179	15.624	
	8.389	3.126	286	26.837	
	10.578	3.051	358	34.670	
0.750	4.632	3.390	156	13.664	8.02
	6.465	3.329	212	19.121	
	8.546	3.248	288	27.262	
1.00	2.207	3.407	77	6.478	8.02
	6.696	3.245	224	20.635	
	8.739	3.184	284	27.447	

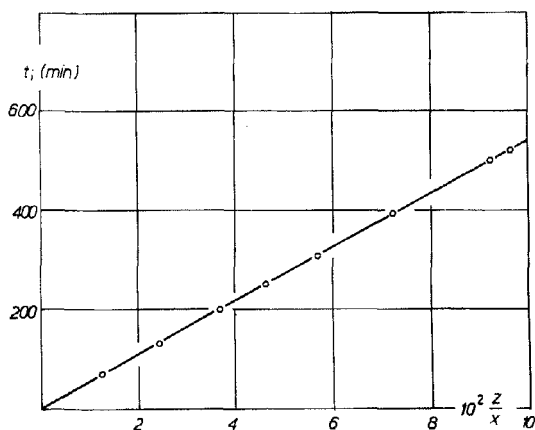


FIG. 2. Dependence of the inhibition period on inhibitor concentration in the system AN/MA/AIBN/DMF/Banfield radical/323°K; $x_{MA} = 0.25 (m_1 + m_2) = 3.8$ mole/L.

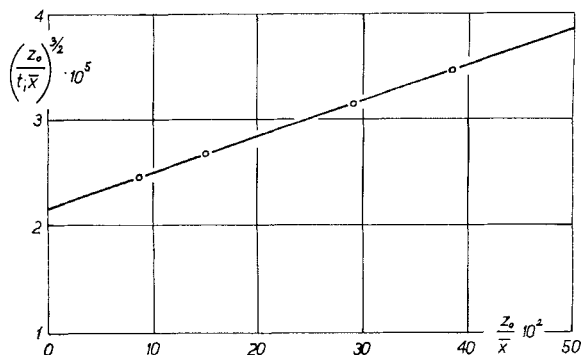


FIG. 3. Experimental data of the system AN/MA/AIBN/DMF/Banfield radical/333° K plotted according to Eq. (2).

$$\left[X_{MA} = \frac{m_{MA}}{m_{MA} + m_{AN}} \right]$$

are shown in Fig. 4.

The figure indicates that the $2k_1f$ values depend slightly on the monomer composition at 313, 323, and 333° K.

Determination of the Rate Constant of Initiator Decomposition

In order to know the efficiency factor (f) of initiation, the rate constant of thermal decomposition of AIBN (k_1) was determined azotometrically at 323 and 333° K in the following systems:

1. Dimethylformamide
2. Acrylonitrile/dimethylformamide mixture ($m_{AN} = 3.8$ mole/L).
3. Methyl acrylate/dimethylformamide mixture ($m_{MA} = 3.8$ mole/L).
4. Acrylonitrile/methyl acrylate/dimethylformamide mixture ($m_{AN} = m_{MA} = 1.9$ mole/L).

The rate constant of initiator decomposition was determined from the slopes of $V_\infty / (V_\infty - V_t)$ vs t curves [18], where V_∞ is the volume of N_2 belonging to total decomposition of the initiator used, and V_t is the volume of nitrogen evolved until the moment t , both in milliliters.

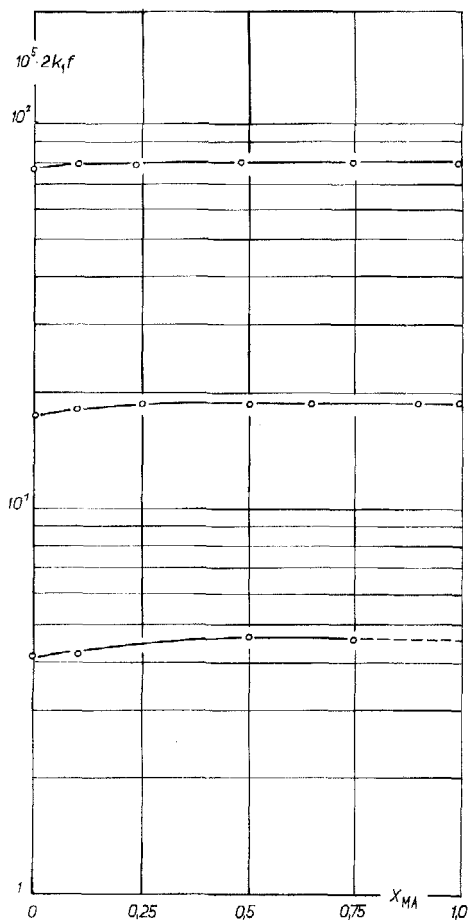


FIG. 4. Dependence of initiation rate constant on monomer composition.

The values of k_1 determined in the above systems are listed in Table 4. It can be seen that the values of k_1 are (within the limit of error) independent of monomer composition at both 323 and 333°K, and they are equal to the value measured in DMF; therefore k_1 was determined at 313°K only in DMF and it gave $3.07 \times 10^{-5} \text{ min}^{-1}$. Using this value and $k_1 = 1.47 \times 10^{-4}$ (at 323°K) and $k_1 = 6.68 \times 10^{-4}$ (at 333°K), from the $2k_1f$ values determined at different compositions

TABLE 4. Rate Constants of AIBN Decomposition in Different Systems

System	$10^4 k_1 (\text{min}^{-1})$	
	323° K	333° K
1	1.49	6.71
2	1.48	6.66
3.	1.47	6.68
4	1.47	6.68

TABLE 5. Dependence of the Efficiency Factor of Initiation on Monomer Composition

313° K		323° K		333° K	
x_{MA}	f	x_{MA}	f	x_{MA}	f
0	0.681	0	0.600	0	0.582
0.1	0.682	0.1	0.622	0.1	0.591
0.5	0.753	0.25	0.637	0.23	0.593
0.75	0.744	0.5	0.640	0.48	0.600
		0.65	0.639	0.75	0.601
		0.9	0.639	1.0	0.600
		1.0	0.638		

(see Tables 1, 2, and 3) the values of radical efficiency (f) were calculated. These data are given in Table 5.

These data show that the value of f is, to some extent, dependent on both monomer composition and temperature. For example, the change amounts to about 10% at 313° K, which cannot be neglected in precise kinetic investigations. With an increase of temperature, the value of f slightly decreases, in accordance with some literature data [19, 20].

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